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SUMMARY REPORT

AN ADHESION CRITERION IN THE GAS SOLID INTERFACE

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ABSTRACT

A theoretical model is developed to establish an adhesion criterion for the interaction of a gas atom or molecule with a nonmetallic surface. As a first approximation a linear lattice mass points of the solid surface is considered and the classical lattice dynamical model is used.

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INTRODUCTION

Classical as well as quantum mechanical approaches[1,2,3] have been developed by different investigators in arriving at satisfactory models for the trapping of gas atoms by solid surfaces. In this investigation the classical approach using the formalism of lattice dynamics is used. As a plausible potential for the interaction between the surface and the impinging atom, the well-known Lennard-Jones[4] potential is used.

The intermolecular interactions are represented by appropriate spring constants; a uniform spring constant for the binding between the atoms of the solid and a different value for the interaction between the incoming gas atoms and the nearest surface atom are used in this approach.

The required adhesion criterion is developed in the form of an estimated potential well depth which is used to compare the kinetic energy of the incident molecules. It is assumed that molecules with energies greater than the well depth will be reflected back whereas those with energies less than this amount will be absorbed.

The one-dimensional semi-infinite lattice model used in the present discussion can be extended to the more realistic three-dimensional situation.

THEORETICAL APPROACH

One dimensional chain lattice

The solid surface can be approximated to a semi-infinite one dimensional lattice with identical point masses at each lattice site holding each other through a potential which can be represented by a suitable spring constant k. The interaction is limited to only the nearest neighbors. Any change in energy at any of the lattice points will be transmitted to nearest neighbor and from that to the next and so on.

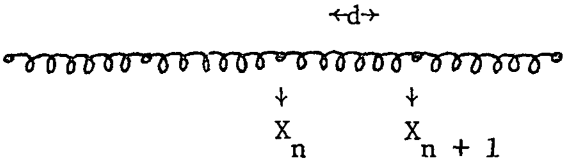


Fig. 1. one dimensional lattice

Let the instantaneous position of the n^{th} and $(n + 1)^{th}$ atom in the chain be denoted by X_n and X_{n+1} respectively. Further, let the equilibrium distance be denoted by d.

Let there be a disturbance in the linear chain by an approaching impurity atom (gas atom) leading to a displacement ϕ_n for the n^{th} atom, thereby bringing the n^{th} atom to its instantaneous position denoted by X_n. Under these circumstances one can write

$$X_n = nd + \phi_n . \qquad 1$$

In a similar manner one can write for the $(n + 1)^{th}$ atom

$$X_{n+1} = (n + 1)d + \phi_n . \qquad 2$$

The interaction energy between the n^{th} and $(n + 1)^{th}$ atom will be a function of the positions and can be represented by a potential function of the form

$$V(x) = V(|X_{n+1} - X_n|). \tag{3}$$

Equation 3 can be rewritten using equations 1 and 2 and one obtains

$$\begin{aligned} V(x) &= V \; |[(n + 1)d + \phi_{n+1}] - [nd + \phi_n]| \\ &= V\,\{d + |\phi_{n+1} - \phi_n|\} \; . \end{aligned} \tag{4}$$

The change in displacements between successive lattice mass points will be much smaller than the mean distance between successive lattice sites.

$$|\phi_{n+1} - \phi_n| \;\ll\; d \; . \tag{5}$$

Therefore, it is reasonable to make a Taylor expansion of the potential function v(x) about x=d which leads to

$$\begin{aligned} V(x) &= V(d) + \frac{\partial v}{\partial x}\Big|_{x=d} \left(|\phi_{n+1} - \phi_n|\right) \\ &+ \frac{\partial^2 v}{\partial x^2}\Big|_{x=d} \cdot \frac{1}{2}\left(|\phi_{n+1} - \phi_n|\right)^2 + \ldots . \end{aligned} \tag{6}$$

In equation 6, v(d) is a constant. Since d is the equilibrium distance, the potential function should be an extremum at x=d. This would mean that,

$$\frac{\partial v}{\partial x}\bigg|_{x=d} = 0. \qquad 7$$

At equilibrium position force is zero. Using the analogy from spring, one can assume a relation of the form fα - kx or $\frac{\partial v}{\partial x}$ αkx. This would imply that at $\frac{\partial^2 v}{\partial x^2}\Big|_{x=d}$ will be a constant. This simplification yields from equation 6.

$$V(x) = C_1 + \frac{1}{2}K(|\phi_{n+1} - \phi_n|)^2 . \qquad 8$$

At the site of the nth atom, there is a similar contribution from the (n-1)th atom. Thus the total potential at the site of the nth atom can be written as

$$V(x) = \frac{1}{2}K(|\phi_{n+1} - \phi_n|)^2 + \frac{1}{2}K(|\phi_n - \phi_{n-1}|)^2 + C. \qquad 9$$

The force on the nth lattice atom is then written as

$$F_n = - \frac{\partial v}{\partial \phi_n}$$

$$= -K(\phi_{n+1} - \phi_n)(-1) - K(\phi_n - \phi_{n-1}). \qquad 10$$

Or $\quad F_n = K(\phi_{n+1} + \phi_{n-1} - 2\phi_n)$.

The corresponding equation of motion is written as

$$m\frac{d^2\phi_n}{dt^2} = K(\phi_{n+1} + \phi_{n-1} - 2\phi_n) . \qquad 11$$

Equation 11 is a representative equation which can be used to study the propogation of energy transfer through a lattice medium. The above considerations can be further simplified by adopting the following notations:

$$\text{Let } \omega_0^2 = \frac{K}{m}; \tag{12}$$

$$\text{And } \tau = \omega_0 t . \tag{13}$$

$$\text{Then, } \frac{d\phi}{dt} = \frac{d\phi}{d\tau} \cdot \frac{d\tau}{dt} = \omega_0 \frac{d\phi}{d\tau}.$$

$$\text{Similarly, } \frac{d^2\phi}{dt^2} = \omega_0 \frac{d}{dt} \left(\frac{d\phi}{d\tau}\right)$$

$$= \omega_0 \frac{d\tau}{dt} \frac{d}{d\tau} \left(\frac{d\phi}{d\tau}\right)$$

$$= \omega_0^2 \frac{d^2\phi}{d\tau^2} . \tag{14}$$

Using equation 14 in equation 11, one obtains for the (n + 1)th particle

$$m\omega_0^2 \ddot{\phi}_{n+1} = K(\phi_{n+2} - 2\phi_{n+1} + \phi_n),$$

$$\text{and} \qquad \ddot{\phi}_{n+1} \doteq \phi_{n+2} - 2\phi_{n+1} + \phi_n . \tag{15}$$

Equation 15 represents the motion of the (n + 1)th atom in terms of the displacement of the nearest neighbors.

When an external impurity atom approaches the zeroth atom, the motion of the coupled system can be written as given in 10 if the relative displacement of the incoming atom is denoted by ξ, and the spring constant representing the coupling between the zeroth atom and the trapped atom is denoted by K_o, then equation 10 leads to ,

$$m\frac{d^2\phi_0}{dt^2} = K(\phi_1 - \phi_0) + K_0(\xi - \phi_0). \qquad 16$$

This is the equation of motion of the zeroth atom on the surface.

$$m\omega_0^2 \frac{d^2\phi_0}{d\tau^2} = K(\phi_1 - \phi_0) + K_0(\xi - \phi_0),$$

$$\text{Or} \qquad \frac{m}{K}\omega_0^2 \frac{d^2\phi_0}{d\tau^2} = (\phi_1 - \phi_0) + \frac{K_0}{K}(\xi - \phi_0). \qquad 17$$

Since $\frac{K}{\omega}$ is defined as ω_o^2, and if one further defines $\frac{K_o}{K}$ as β, equation 17 reduces to

$$\ddot{\phi}_0 = (\phi_1 - \phi_0) + \beta(\xi - \phi_0). \qquad 18$$

The motion of the impurity atom alone can be described by

$$m_0 \frac{d^2\xi}{dt^2} = K_0(\phi_0 - \xi),$$

$$\text{Or} \qquad \frac{m_0}{K}\omega_0^2 \ddot{\xi} = \frac{K_0}{K} m(\phi_0 - \xi),$$

$$\text{Or} \qquad m_0 \ddot{\xi} = \beta m(\phi_0 - \xi). \qquad 19$$

If one writes $m_0/m = \mu$, equation 19 reduces to

$$\mu\ddot{\xi} = \beta(\phi_0 - \xi) = \beta y(\tau).$$

One then rewrites equation 18 in terms of equation 20 to obtain

$$\ddot{\phi}_0 = (\phi_1 - \phi_0) + \mu\ddot{\xi}, \qquad 21$$

$$y(\tau) = \phi_0(\tau) - \xi(\tau)$$

and
$$\ddot{y} = \ddot{\phi}_0 - \ddot{\xi}. \qquad 22$$

Equation 21 can be rewritten in terms of 20 as

$$\ddot{\phi}_0 = (\phi_1 - \phi_0) + \beta y(\tau). \qquad 23$$

Equation 23 when applied in equation 22 one obtains

$$\ddot{y} = (\phi_1 - \phi_0) + \beta y(\tau) - \ddot{\xi}(\tau)$$

$$= (\phi_1 - \phi_0 + \beta y(\tau) - \frac{\beta}{\mu} y(\tau), \qquad 24$$

Or $$\ddot{y}(\tau) = (\phi_1 - \phi_0) - \beta\left(\frac{\mu + 1}{\mu}\right) y(\tau); \qquad 25$$

Or $$\ddot{y}(\tau) + \beta\left(\frac{\mu + 1}{\mu}\right) y(\tau) = \phi_1 - \phi_0. \qquad 26$$

Equation 26 represents coupled equation of motion. This is similar to a harmonic equation with a forcing term. At this stage it is convenient to revert the variables back in terms of real time.

$$\frac{1}{\omega_0^2} \frac{d^2y}{dt^2} + \beta\left(\frac{\mu + 1}{\mu}\right)\frac{1}{\omega} y = \phi_1 - \phi_0 . \qquad 27$$

Let $$\Omega^2 = \omega_0^2 \quad \beta\left(\frac{\mu + 1}{\mu}\right) \qquad 28$$

and $$\omega_0^2 \; (\phi_1 - \phi_0) = f(t).$$

Equation 27 is now rewritten as

$$\frac{d^2y}{dt^2} + \Omega^2 y = f(t). \qquad 29$$

The factor which modifies the free lattice frequency is $\{\beta[(\mu+1)/\mu]\}^{1/2}$ and this is the effect of the coupled external molecule. Equation 28 is a harmonic equation with a forcing term and the forcing function is $f(t) = \omega_0^2 (\phi_1 - \phi_0)$.

TRAPPING ENERGY

Molecular potentials

In a simple classical model, the molecular interaction potential can be expressed by various different potentials such as Lennard-Jones[4] which is usually written as

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \qquad 30$$

where r is the distance from the surface lattice atom, σ is the distance of closest approach by the incoming atom and ε is the depth of the potential.

A more realistic potential would be the Buckingham[5] potential which includes the induced dipole-induced dipole interaction and the induced dipole-induced quadrupole interactions. Buckingham potential is usually written as

$$\Phi(r) = be^{-ar} - cr^{-6} - e' r^{-8} . \qquad 31$$

While it is a more realistic potential than the Lennard-Jones (6-12) potential, it is more difficult to handle. A third potential which is flexible and often used in calculations is the Modified Buckingham (6-Exp)[6] potential which has the form

$$\Phi(r) = \frac{\varepsilon}{1-\frac{6}{\alpha}} [\frac{6}{\alpha}\exp([1 - \frac{r}{rm}]) - (\frac{rm}{r})^6] \qquad r \geq r_{max}$$

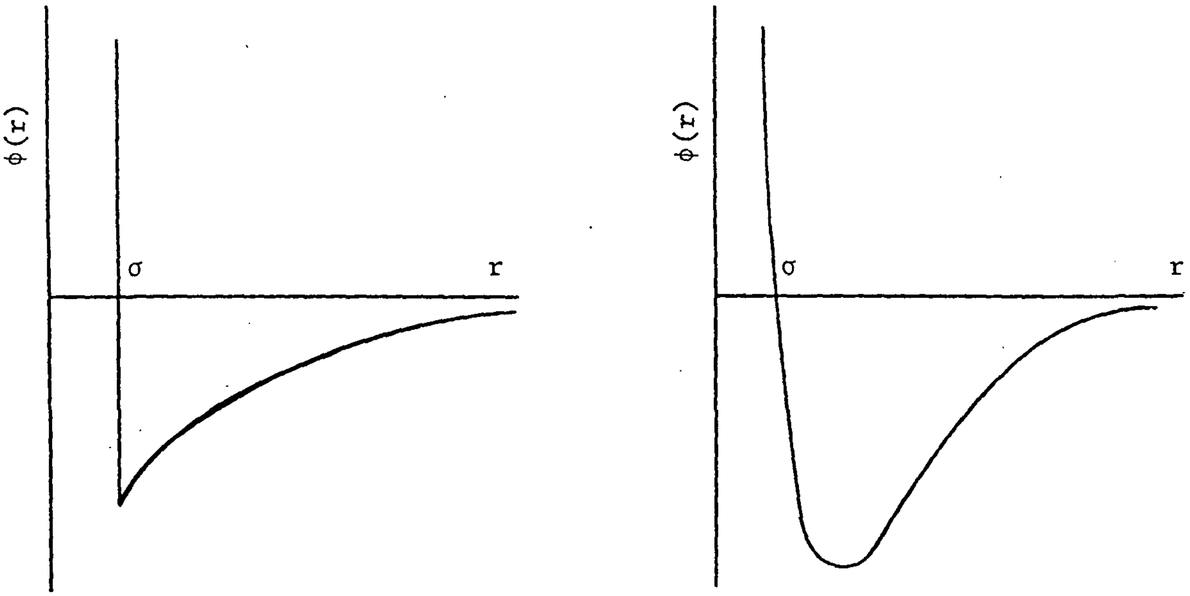
$$\Phi(r) = \alpha \cdot \qquad r << r_{max} \qquad 32$$

This is somewhat more flexible than the Lennard-Jones potential since it permits the variation of the low velocity collision diameter. Another potential often encountered in literature is the Stockmayer Potential[7] which is a superposition of the Lennard-Jones potential.

$$\phi(r, \theta_a, \theta_b, \phi_b - \phi_a) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] - \frac{\mu_a \mu_b}{r^3} g(\theta_a,\theta_b,\phi_b,-\phi_a). \qquad 33$$

The last term in the expression on the right-hand side of equation 33 accounts for the angular dependence of the dipole-dipole interaction.

This potential describes well the interaction between such polar molecules for which dipole-quadrupole and higher multipole interactions are not important.



a. Southerland model b. Lennard-Jones potential

Fig. 2. Spherically symmetric potentials

The interaction of an adsorbed impurity atom by a solid surface, it is assumed, can be best described by the Lennard-Jones potential which is shown in Fig. 2b. The potential itself is described by equation 29. It can be reasonably assumed from the shape of the potential, that the intercept σ can be taken as the distance of closest approach for an external molecule. One further makes the stipulation that the depth of the potential well, ε, can be interpreted as the mean binding energy of an incoming atom when it is absorbed. Under these circumstances, it is reasonable to assume that an incoming molecule will be trapped if it comes closer than the mean distance of closest approach and if the magnitude of its kinetic energy is less than the potential depth. This is a classical concept. It must be noted that the interaction potential does not become a trapping potential until the approaching molecule is closer than R_B where R_B is shown in Fig. 2b.

An estimate of trapping energy

Equations 28 and 29 may now be used to estimate the trapping energy E_B as follows. A simplifying assumption that one can make is that the lattice response forcing function, which is given by

$$f(t) = \omega_0^2 (\phi_1 - \phi_0),$$

is small compared to the relative acceleration $\frac{d^2y}{dt^2}$ and the average displacement $\Omega^2 y$. This would lead to further simplifying situation that the system would oscillate essentially with free angular frequency Ω. Further, if one approximates equation 29 to be of harmonic form, which can be written in the form

$$V' = 1/2\kappa\eta^2 \qquad 34$$

where κ is an equivalent spring constant which is related to

$$\Omega^2 = \frac{\kappa}{m_0} . \qquad 35$$

The approximated Lennard-Jones potential and the modified harmonic potential are shown in Fig. 3.

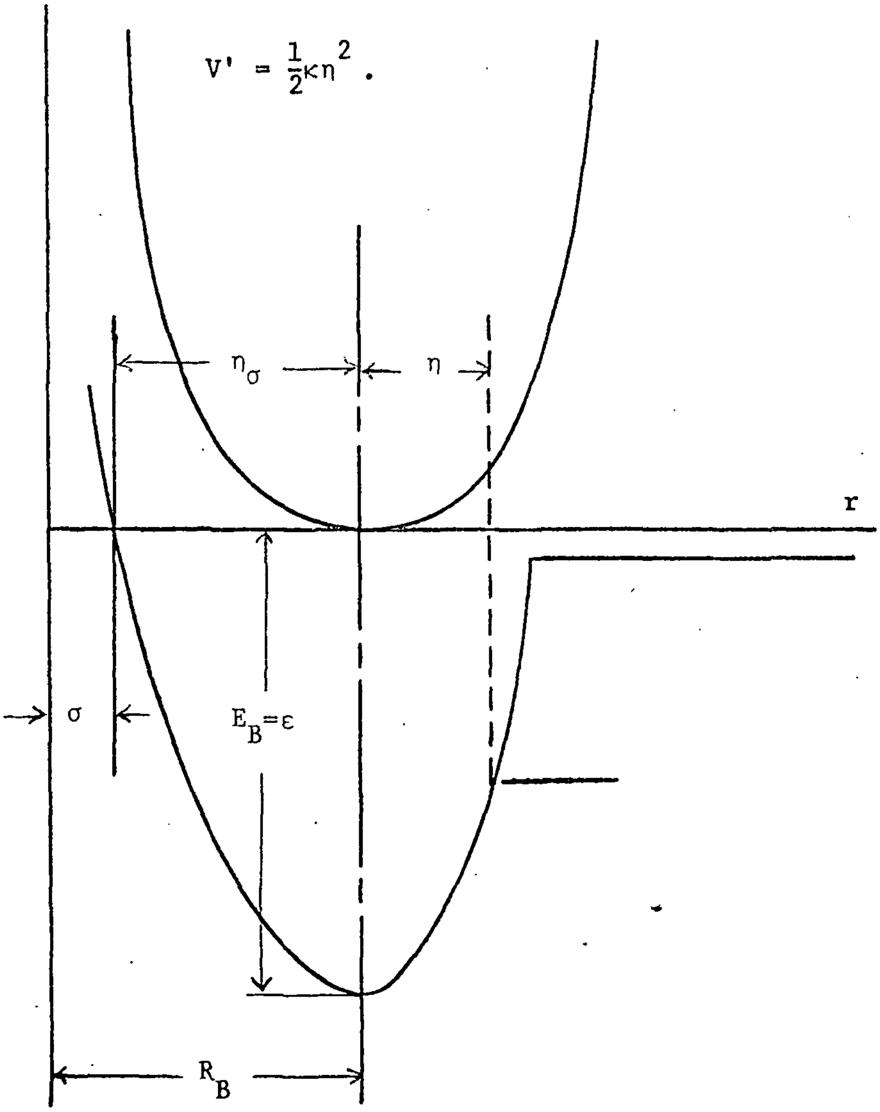


Fig. 3. Approximate harmonic well potential

Obviously one can then write the expression for the lower potential (Fig. 3) in terms of the harmonic potential as

$$V = V' - E_B \,. \qquad 36$$

Using equation 34 in 36 and evaluating the potential for the lower curve (Fig. 3) for r is equal to σ, one obtains

$$0 = \frac{1}{2}\kappa\eta_\sigma^2 - E_B \,. \qquad 37$$

$$E_B = \frac{1}{2}\kappa\eta_\sigma^2 \,. \qquad 38$$

One makes use of the relations given in equations 28 and 35 to reduce equation 38. Thus,

$$\kappa = m_0 \Omega^2 = m_0 \omega^2 [\beta(\frac{\mu + 1}{\mu})]. \qquad 39$$

From Fig. 3,

$$\eta_\sigma = R_B - \sigma \,. \qquad 40$$

The use of equations 39 and 40 in equation 38 leads to,

$$E_B = \frac{1}{2} m_0 \omega_0^2 [\beta(\frac{\mu + 1}{\mu})](R_B - \sigma)^2 \,. \qquad 41$$

Obviously, equation 41 is an expression for the binding energy in terms of the quantities on the right hand side of equation; where m_0 is the mass of the trapped molecule, ω_0, which is equal to $(\frac{K}{m})^{1/2}$, is the frequency term, K being the lattice spring constant, m the mass of lattice atom; β is the ratio K_0/K where K_0 is the equivalent spring constant between the trapped atom and the surface atom; μ or $\frac{m_0}{m}$ is the ratio of the masses of trapped and surface atoms; R_B the mean molecular trapping distance and σ is the distance of closest approach.

It is obvious that if the quantities on the right hand side of equation 41 can be evaluated that would provide the necessary information on the probability of adsorption of an incoming molecule by a known target surface.

Distance of closest approach

In the preceding discussion several simplifying assumptions have been made in order to arrive at an expression for the trapping or binding energy E_B as given in equation 41. The more important parameters which are to be determined to evaluate E_B are σ, the distance of closest approach; R_B, the mean molecular trapping distance; and K_0, the intermolecular spring constant between the trapped atom and the surface atom. One makes further simplifying assumptions to evaluate these quantities. The quantity σ which is the collision diameter can be reasonably defined to be the distance of closest approach between two colliding molecules. The value of r, occurring in the Lennard-Jones potential expression, for which $\phi(r)$ becomes zero, will be a measure of σ. The collision diameter is related to the molecular co-volume 'b_0' through the relation,

$$b_0 = \frac{2}{3}\pi\tilde{N}\sigma^3. \qquad 42$$

An alternate method to evaluate σ is to use the diffusion data for molecules. However, the results obtained thus are in reasonable agreement with values obtained from the molecular co-volume as given in equation 42.

In published literature there are available values of molecular co-volume and σ of various molecules. Table 1 is adopted from Curtiss and Herschfelder to show some typical values of these quantities.

Compound	σ (A°)	b_0 cc/mole
$CHCl_3$	2.98	33.45
$CHCl_2F$	4.82	141.0
C_2H_5Cl	5.41	199.7
H_2O	2.65	23.45
NH_3	2.60	22.12

Table 1

Sample Values of σ and b_0

In terms of the constants appearing in equation 42, one can express molecular co-volume as

$$b_0 = 1.26515\sigma^3.$$

The trapping distance R_B is of interest here now. From Fig. 3, it is seen that when r is equal to R_B,

$$V(r) = V(R_B) = -\varepsilon = -E_B. \qquad 43$$

This information can be used in the Lennard-Jones potential

$$V(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6].$$

From equation 43, this becomes

$$-\varepsilon = 4\varepsilon[(\frac{\sigma}{R_B})^{12} - (\frac{\sigma}{R_B})^6]. \qquad 44$$

Equation 44 leads to quadratic of the form

$$(\frac{\sigma}{R_B})^{12} - (\frac{\sigma}{R_B})^6 + \frac{1}{4} = 0. \qquad 45$$

Or

$$[(\frac{\sigma}{R_B})^6 - \frac{1}{2}]^2 = 0.$$

This leads to two equal roots

$$(\frac{\sigma}{R_B})^6 = \frac{1}{2}. \qquad 46$$

This leads to a solution

$$R_B = (2)^{1/6}\sigma,$$

or

$$R_B = 1.122\sigma. \qquad 47$$

When the value of R_B from 47 is used in equation 41, one obtains for binding energy

$$E_B = \frac{1}{2} m_0 \omega_0{}^2 [\beta(\frac{\mu+1}{\mu})] (.122\sigma)^2. \qquad 48$$

It remains to calculate the spring constants K between the lattice mass points of the target and K_0, the similar parameter relating the incident molecule to the surface atom. In the latter case, where Lennard-Jones potential is adopted, Curtiss and Herschfelder have elaborately discussed the applicability of thermal diffusion data in conjunction with ordinary diffusion data to determine σ and ε which occur in Lennard-Jones potential which describes the interaction of a pair of dissimilar molecules. On the other hand, this can be treated as a dipole-dipole interaction in which case the force of attraction can be written as

$$F_{12} = -6 \frac{\mu_1 \mu_2}{r^4} \qquad 49$$

where μ_1 and μ_2 are the dipole moments and r the mean distance. Since we have replaced this force by a spring, equation 49 can be written as

$$F_{12}(R_s) = K_0 R_s \qquad 50$$

where R_s is the separation distance at which the attractive potential of the surface atom is experienced by the incoming molecule.

Equations 49 and 50 immediately lead to the result

$$K_0 \sim \frac{6\mu_1\mu_2}{{R_s}^5}. \qquad 51$$

μ_1 and μ_2, the induced dipole moments, can be evaluated from molecular data. The separation distance R_s can be approximated from the shape of the potential in terms of η_σ and σ. From fig. 3 one can write

$$R_s = 2\eta_\sigma + \sigma = 2R_B - \sigma.$$

Finally, the lattice spring constant can be obtained from the properties of the material. Thus for example the speed of sound in a material is given by

$$v = (\frac{y}{\rho})^{1/2},$$

where y is Young's modulus, and ρ the density. Using the relation between ω and v the frequency, one can then write

$$v = \lambda\omega,$$

where λ is the wave length. In the linear approximation of a spring type force between the atoms, then one can write

$$\omega = \frac{\sqrt{K}}{\sqrt{m}}$$

$$\text{or} \qquad K = m\omega^2$$

$$= m\left(\frac{v}{\lambda}\right)^2.$$

Thus the various quantities appearing in equation 48 are evaluated to obtain an estimate of the trapping energy.

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